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Spectrophotometric Determination of Uranium by Solvent Extraction as Acetylacetonate

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Spectrophotometric determination of uranium, based on the extraction of uranyl acetylacetonate, was investigated. Uranyl acetylacetonate was nearly quantitatively extracted with butyl acetate at pH 6.5~7.0. The extracted chelate seemed to be an addition compound having a composition of $\text{UO}_2(\text{C}_6\text{H}_7\text{O}_2)_2 \cdot \text{C}_8\text{H}_8\text{O}_2$, and its absorption spectrum showed a maximum at $365\text{m}\mu$. The colour was stable, Beer's law was valid up to 70 ppm of uranium and molar extinction coefficient, obtained at $365\text{ m}\mu$, was about 2640 (L/M cm.). Titanium, chromium, manganese, ferric iron and large amounts of copper interfered the determination, but molybdenum, vanadium, tungsten *etc.* did not interfere.

INTRODUCTION

In the previous paper¹⁾, the extraction method of uranium was investigated, where uranium was extracted as its acetylacetonate with chloroform. Uranium acetylacetonate is more easily extracted with butyl acetate rather than with chloroform. The chelate shows absorption band in near ultraviolet region, in the solvent as well as in the aqueous medium, and it can be adapted to the photometric determination of uranium. Already, the photometric method, used for aqueous medium, was proposed by Shigematsu and the author²⁾. In the present paper, the detailed conditions for the spectrophotometric determination of uranium by solvent extraction, were described.

APPARATUS AND MATERIALS

Apparatus

Spectrophotometric measurements were made with Hitachi's Photoelectric Spectrophotometer, Model EPU-2A, using 1.0 cm. silica transmission cells, and Horiba's Glass electrode pH meter, Model, M-3 was used for the pH measurements.

Materials

Standard solution of uranium, $100\text{ }\mu\text{g./ml.}$; a stock solution was prepared by dissolving $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in water, and its concentration was determined by the gravimetric method as U_3O_8 . The stock solution was diluted to make a

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standard solution containing 100 μg . of uranium in each milliliter.

5 % Acetylacetone solution ; 25 g. of acetylacetone were dissolved and diluted to 500 ml. with water.

10 % EDTA solution ; 25 g. of disodium salt of ethylenediaminetetraacetic acid were dissolved in water and made up to 250 ml..

Calcium chloride solution ; 10.75 g. of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ was dissolved in water and made up to 250 ml. The solution is equivalent to 10 % EDTA solution.

Butyl acetate, ethyl acetate and chloroform ; these solvents were washed with dil. NaOH solution, water, dil. HCl solution and three successive portions of water and then distilled.

Uranium acetylacetonate. Uranium acetylacetonate was prepared according to Krishen's method. An aqueous solution of uranium nitrate, containing excess acetylacetone, was made ammoniacal. The resulting yellow precipitate of acetylacetonate was recrystallized from hot ethyl alcohol.

For the air-dried crystal, the following analytical data were obtained.

	Found (%) (mean value of duplicate analysis.)	Calculated (%) for $\text{UO}_2(\text{A.A.})_2$	Calculated (%) for $\text{UO}_2(\text{A.A.})_2\text{A.A.}$
Uranium	42.05	50.84	41.90
Carbon	30.10	25.86	31.69
Hydrogen	3.93	3.02	3.90

From the analytical results, uranium acetylacetonate obtained, may be an addition compound whose formula is $\text{UO}_2(\text{C}_5\text{H}_7\text{O}_2)_2 \cdot \text{C}_5\text{H}_8\text{O}_2$.

EXPERIMENTAL

I. Absorption Spectra of Uranium Acetylacetonate in Organic Solvents

Prior to the experiments on the extraction, the absorption spectra of the organic solutions of uranium acetylacetonate, prepared by dissolving the uranium acetylacetonate, were obtained.

As uranium chelate was hardly soluble in butyl acetate, ethyl acetate or in chloroform, in the absence of excess acetylacetone, the solvents containing different amount of acetylacetone were used.

The absorption curves for $2 \times 10^{-4}M$ uranium acetylacetonate, measured against the reagent blank, were shown in Fig. 1 and Fig. 2.

From the figures, it is evident that the absorption spectra of the chelate in chloroform are considerably affected with the concentration of excess acetylacetone, while the spectra obtained in ester media are not influenced at all with the excess reagent. And the maximum absorption coefficient obtained, in esters, was larger than that in chloroform. Therefore, esters were found to be suitable solvent for analytical purpose, and butyl acetate seemed to be better than ethyl acetate, because of its insolubility in water. So, in further experiments, butyl acetate was used as a solvent.

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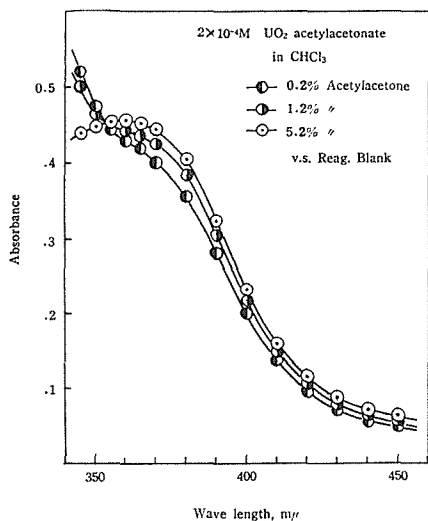


Fig. 1. Absorption spectra of uranyl acetylacetonate in chloroform.

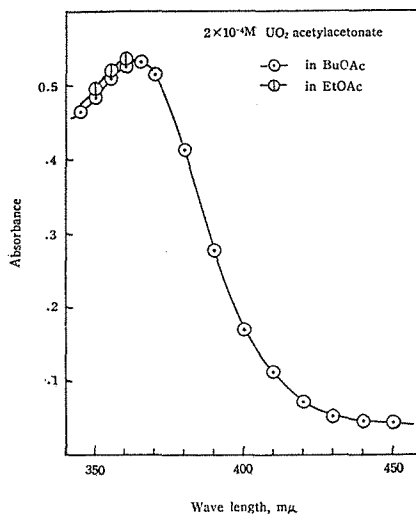


Fig. 2. Absorption spectra of uranyl acetylacetonate in esters.

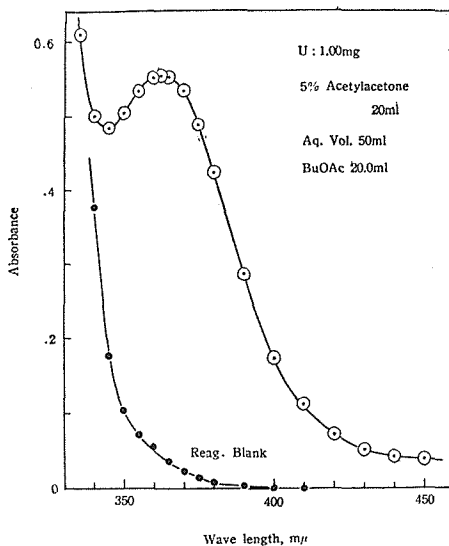


Fig. 3. Absorption spectrum of uranium acetylacetonate, extracted.

Fig. 3 presented the absorption spectrum of the uranium acetylacetonate solution which was obtained by the following procedure.

To the solution of uranium nitrate (1 mg. of uranium), 20 ml. of 5 % acetylacetonate solution was added, and its pH was adjusted to 7.0. After diluted to about 50 ml., uranium acetylacetonate was extracted with 20.0 ml. of butyl acetate, and absorbance of the organic solution was measured against the reagent blank.

As shown in the figure, the shape of the spectrum is quite similar to that of curve A in Fig. 2.

The colour of uranium acetylacetonate in butyl acetate did not change for 24 hours, at least.

II. Effect of Concentration of Acetylacetonate

In order to investigate the effect of reagent concentration, the extractions were made with the sample solutions containing 1 mg. of uranium and different amount of acetylacetonate. Absorbance was measured against the reagent blank, at 365 and 400 $m\mu$. The results were shown in Fig. 4. The concentration of the reagent has not any effect on the absorbance of the chelate, if it is more than 0.1 percent.

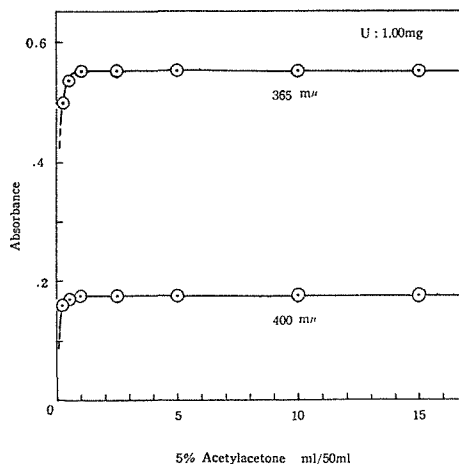


Fig. 4. Effect of concentration of acetylacetonate.

III. Effect of pH Value

The effect of pH value was investigated, using 2 ml. of 5% acetylacetonate

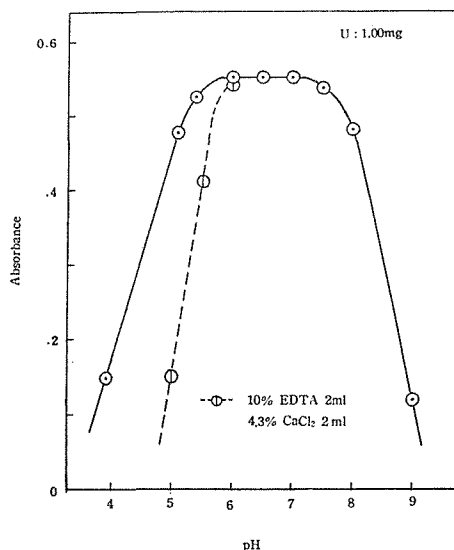


Fig. 5. Effect of pH value.

Spectrophotometric Determination of Uranium by Solvent Extraction as Acetylacetonate solution per 50 ml. of the aqueous solution containing 1 mg. of uranium. As shown by curve A in Fig. 5, optimum pH region is from 6.0 to 7.0 for the determination of uranium.

IV. Effect of Ethylenediaminetetraacetic Acid

In order to prevent the interference of the diverse ions, EDTA was introduced as a masking agent. As previously reported¹⁾, the extractability of uranium acetylacetonate was decreased by the addition of EDTA, and in the present condition, the extraction could not be recovered even by the use of sodium chloride as shown in Table I. This fact might be due to the low concentration of acetylacetone. So it was examined that calcium was used as the demasking agent.

Table 1. The effect of NaCl.

U : 500 μ g. ; pH 7.0 ; 10 % EDTA solution 2 ml. ; 5 % acetylacetone solution 2 ml.

NaCl added (g).	365 m μ	Absorbance 400 m μ
0	0.044	0.014
2.5	.095	.034
5.0	.106	.035
7.5	.108	.037
10.0	.114	.039
In the absence of EDTA	.276	.087

When 2 ml. of 10 % EDTA solution and equivalent of calcium chloride solution were added, the absorption spectrum showed a good agreement with that obtained without the use of EDTA. If EDTA is consumed for the masking of other ions which form more stable complexes with EDTA, some calcium will be present as free ion. Considering this case, it was confirmed that the presence of excess calcium ion did not affect the absorption spectrum.

Curve B in Fig. 5 indicated the relationship between pH value and absorbance, which was obtained in the presence of EDTA and calcium chloride. Experimental data fall on the curve A, when pH value is above 6. This shows that uranium is completely demasked from EDTA, as above mentioned. On the other hand, at pH below 6, the large deviation of curve B from A indicates that calcium-EDTA complex is less stable than uranium complex, in such pH region.

V. Spectrophotometric Procedure for the Determination of Uranium

From the foregoing experimental results, the procedure for the spectrophotometric determination of uranium was established as follows.

To the sample solution containing 200 μ g.~1500 μ g. of uranium, add 2 ml. of 10 % EDTA and its equivalent amount of calcium chloride solution, and adjust the pH to about 7. Add 2 ml. of 5 % acetylacetone solution, adjust the pH to 6.5~7.0 again, and dilute to about 50 ml. with water. Transfer the solu-

tion into a 100 ml. separating funnel and extract uranium acetylacetonate with 20.0 ml. of butyl acetate. Obtain the organic layer, dehydrate with sodium sulphate anhydrous, and then measure the absorbance at 360 or 365 $m\mu$ against the reagent blank.

Calibration curve, obtained by the procedure, is shown in Fig. 6. Beer's law is followed up to 70 ppm. of uranium and molar extinction coefficient of this color system is about 2640 (L/M cm) at 360 or 365 $m\mu$.

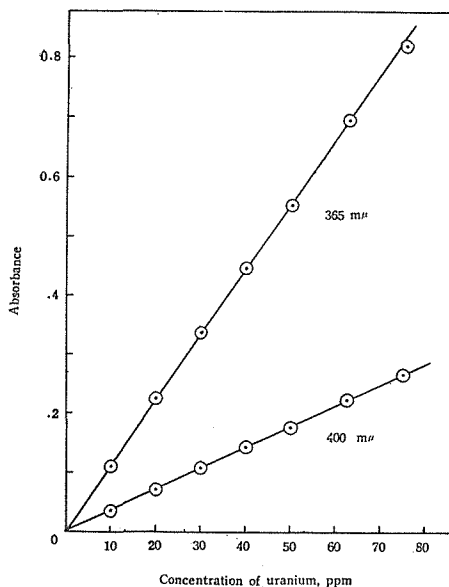


Fig. 6. Calibration curves.

VI. Diverse Ions

To study the influence of several metal ions, measurements were carried out for the solution containing a proper amount of foreign cations with 500 μg . of uranium. The results are summarized in Table 2.

Ten milligrams of Ag^+ , Al^{3+} , Bi^{3+} , Cd^{++} , Co^{++} , Mg^{++} , Mo^{6+} , Ni^{++} , Pb^{++} , V^{5+} , W^{6+} , Zn^{++} and alkali earths did not interfere. Titanium (IV) and chromium (III) interfered owing to the formation of hydroxide, and large amount of ferric iron was also precipitated as acetylacetonate, even when EDTA was added. Cupric, manganese and ferric* ions gave positive error due to the coloration in solvent layer. These cations except cupric must be absent and for copper, the maximum allowable amount was 2 mg..

VII. Recovery of Uranium by the Extraction

For the application of the method recommended for the determination to

* Ferric iron can be separated from uranium, when the extraction of acetylacetonate was previously made at pH 4 with chloroform. This will be discussed in a further paper, together with the simultaneous determination of iron and uranium.

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Table 2. Influence of diverse ions.

Name	Diverse ion added (mg).	as	U found* (μg).		Remark
			365 $m\mu$	400 $m\mu$	
Ag ⁺	10	nitrate	472	488	**
Al ³⁺	10	nitrate	498	500	**
Ba ⁺⁺	10	chloride	500	500	**
Bi ³⁺	10	nitrate	500	500	
Cd ⁺⁺	10	sulphate	500	500	**
Co ⁺⁺	10	sulphate	498	500	
Cu ⁺⁺	10	sulphate	691	785	a)
	2		506	505	b)
Fe ³⁺	10	chloride	—	—	a)
	2		—	—	c)
Mg ⁺⁺	10	sulphate	502	500	**
Mn ⁺⁺	10	sulphate	871	—	d)
	2		538	588	d)
Mo ⁶⁺	10	Na molybdate	448	449	
	10		493	488	***
Ni ⁺⁺	10	sulphate	498	500	
Pb ⁺⁺	10	nitrate	498	500	
V ⁵⁺	2	NH ₄ metavanadate	502	500	
	10		498	500	***
W ⁶⁺	10	Na tungstate	458	460	
	10		494	494	***
Zn ⁺⁺	10	sulphate	500	494	**

* U present 500 μg .

** Absorbances were obtained in the absence of EDTA.

*** 3 ml. of 5 % acetylacetone solution was used.

a) Acetylacetonates precipitated.

b) Blue colour developed in solvent layer.

c) Red colour developed in solvent layer.

d) Yellow colour developed in aqueous and in solvent layer.

the separation of uranium, extraction was made with 10+5+5 ml. of 1% acetylacetone-butyl acetate solution. The extraction yield of uranium in the procedure was obtained by thiocyanate method after the decomposition of organic matters, and it was confirmed that 98~100% of uranium could be recovered by the extraction with butyl acetate.

DISCUSSION

The recommended method for the determination of uranium has several advantages. 1) Although the sensitivity is slightly less than that of thiocyanate method, colour of acetylacetonate is much more stable and reproducible, 2) it is not necessary to keep the reagent concentration at constant, and 3) the effect of diverse cations is little, especially molybdenum, vanadium and tungsten do not interfere.

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For the determination of uranium, butyl acetate is a better solvent than chloroform, as previously mentioned, but for the separation of uranium, each of them has its advantage. That is, by the extraction with butyl acetate, good recovery can be obtained even in low concentration of acetylacetone, while with chloroform, the procedure is much simpler, because its density is greater than unit.

SUMMARY

A spectrophotometric method for the determination of uranium was described. Uranium was extracted with butyl acetate as its acetylacetonate, from the solution having pH of 6.5~7.0.

Effect of the reagent concentration, pH value, EDTA and diverse ions were investigated.

Recovery of uranium by liquid-liquid extraction was also determined.

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- (2) T. Shigematsu and M. Tabushi, *Japan Analyst*, 8, 253 (1959).